Manitoba
Environment
and Workplace
Safety and Health

AMBIENT SULPHUR DIOXIDE AND SULPHURIC ACID MIST LEVELS IN THE VICINITY OF BORDER CHEMICAL COMPANY LIMITED, WINNIPEG, MANITOBA

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Abstract

At the request of the Air Pollution Control Section of Environmental Control Services, operators of the Mobile Monitoring Unit carried out a study to determine ambient ground level concentrations of sulphur dioxide and sulphuric acid mist in the vicinity of Border Chemical Company Limited, Winnipeg, Manitoba during July 1984. Results from this study indicate that contaminant levels in the vicinity, primarily arising from plant emissions, could exceed Manitoba Ambient Air Quality criteria in the vicinity of the plant under the prescribed meteorological conditions.

TABLE OF CONTENTS

	PAGE
ABSTRACT	i
TABLE OF CONTENTS	ii
LIST OF TABLES AND FIGURES	iii
1. Background	1
2. Manitoba Air Quality Objectives and Guidelines	3
2.1 Sulphur Dioxide	3
2.2 Sulphuric Acid Mist	4
3. Procedures	6
3.1 Sulphur Dioxide	6
3.2 Sulphuric Acid Mist	6
3.3 Wind Speed and Direction	6
4. Monitoring Sites	7
5. Results	8
6. Discussion	14
7. Conclusions	16
References	17
Appendices	18

LIST OF TABLES AND FIGURES

TABLES		PAGE
1.	Ambient Air Quality Criteria.....	5
2.	Monitoring Results.....	9
3.	Data Summary (a).....	13
4.	Data Summary (b).....	13

1. BACKGROUND

Border Chemical Company Limited, located at the corner of Day Avenue and Gunn Road, Winnipeg, Manitoba, operates a plant for the manufacture of industrial grade sulphuric acid (H_2SO_4) from high purity elemental sulphur (99.984%). The plant has a rated capacity of 408 tonnes/day, although production can be increased to 454 tonnes/day without significant loss of conversion efficiency.

Elemental sulphur is shipped to the plant in railway tank cars. The sulphur is stored in a large underground tank, where steam is used to keep it in a molten state, allowing impurities to settle out. The molten sulphur is filtered and then pumped into a furnace, where it is burned with dried air to form sulphur dioxide gas (SO_2). Water is removed from the gas by passing it through a drying tower containing sulphuric acid.

The hot gaseous mixture, containing 7 to 11 percent SO_2 by volume, is cooled in a waste heat boiler, which produces steam. The gases are then passed through a catalytic converter containing vanadium pentoxide (V_2O_5), which oxidizes SO_2 to sulphur trioxide (SO_3).

The sulphur trioxide - air mixture is further cooled to permit efficient absorption in sulphuric acid. The mixture passes into an absorption tower, where it is absorbed by water in a 98 percent acid stream, yielding 98.5 percent sulphuric acid.

Exhaust gases from the absorption tower may contribute emissions into the atmosphere. These discharge gases may contain unreacted sulphur dioxide, trace amounts of sulphur trioxide, and sulphuric acid mist.

Stack sampling surveys of emission levels from the Border Chemical plant have been performed. In 1978 and 1979 sulphur dioxide and sulphuric acid mist emissions were found to be in compliance with Clean Environment Commission Order No. 730VC, limiting sulphur dioxide gas and sulphuric acid mist emissions to 13.5 kg/tonne and 0.25 kg/tonne respectively.[1,2] Further testing in July, 1984, yielded similar results.[3]

At the request of the Air Pollution Control Section of Environmental Control Services, a study was undertaken utilizing the Mobile Monitoring Unit downwind of the plant.

Sampling was performed during selected days as meteorological conditions permitted, and as access to affected areas allowed.

Specific objectives of this study were:

1. To determine ambient ground level concentrations of sulphur dioxide and sulphuric acid mist in the vicinity of the plant.
2. To compare concentration levels to Manitoba Ambient Air Quality Objectives/Guidelines, where applicable.

The following sections summarize applicable air quality objectives, sampling and monitoring procedures used, results and a discussion of data obtained.

2. MANITOBA AIR QUALITY OBJECTIVES AND GUIDELINES

Manitoba Air Quality Objectives and Guidelines have been formulated for various air pollutants. The limits for sulphur dioxide and suspended particulate have been adopted from the National Air Quality Objectives, while allowable levels for sulphuric acid mist are Provincial guidelines. (See Table 1).

The provincial criteria have been established for two levels:

Maximum Acceptable Level (MAL) - This level is intended to provide adequate protection against effects on soil, water, vegetation materials, animals visibility, personal comfort and well being.

Maximum Desirable Level (MDL) - This level defines long term goals for air quality and provides a basis for anti degradation policy for the unpolluted parts of the province for the continuing development of control technology.

2.1 Sulphur Dioxide

Background levels of sulphur dioxide in the atmosphere have been determined as 4 micrograms per cubic metre ($\mu g/m^3$) or less, and no current evidence indicates that these levels can cause harm to the environment.[4] Levels well in excess of background concentrations can, however, have a deleterious effect on vegetation and human health.

The maximum acceptable levels have been determined on the basis of the following considerations:

Levels of less than 900 $\mu g/m^3$ (0.34 ppm) average for one hour will help prevent discomfort to sensitive individuals, with respect to taste and odour, and will prevent the persistence of concentrations of SO_2 for several hours, which has the potential to injure vegetation.

Levels of less than 300 $\mu g/m^3$ (0.11 ppm) averaged over 24 hours will help prevent health effects, while levels of less than 60 $\mu g/m^3$ (0.02 ppm) averaged over one year will minimize chronic effects in forests.

The maximum desirable levels have been justified on the basis of being at or below the threshold of very slight human effects and very slight chronic effects to forests.

2.2 Sulphuric Acid Mist

Sulphuric acid mist in the atmosphere has been determined to have a deleterious effect on ecological systems, damaging vegetation and killing certain animal species.[5] This compound is also found to cause corrosion of metals and leaching of construction materials such as limestone and marble.[6] However, the most important effect of sulphuric acid is in the area of human health, with studies indicating that continued exposure causes increased resistance to pulmonary flow and suppressed central nervous system response.[7]

Guidelines for a maximum acceptable ambient level for sulphuric acid mist are set at 100 $\mu g/m^3$ based upon a one hour time weighted average.

TABLE 1 - AMBIENT AIR QUALITY CRITERIA

CONTAMINANT	AVERAGING PERIOD	MAX. DESIRABLE LEVEL	MAX. ACCEPTABLE LEVEL
Sulphur Dioxide	1-hour	450 (0.17)	900 (0.34)
	24-hour	150 (0.06)	300 (0.11)
	Annual	30 (0.01)	60 (0.02)
Sulphuric Acid Mist	1 hour		100

Concentrations are expressed in units of micrograms of contaminant per cubic metre ($\mu g/m^3$) of air corrected to standard conditions of 25°C and 101.3 kilopascals of pressure. The part per million - ppm - (by volume) equivalent concentrations are given in parentheses.

3. PROCEDURES

3.1 Sulphur Dioxide (SO_2)

Monitoring for sulphur dioxide was performed using a Thermo Electron Model 43 pulsed fluorescence ambient SO_2 analyzer. Pulsating ultraviolet light is focused through a narrow band pass filter into a fluorescence chamber. Sulphur dioxide molecules are excited to a higher energy state in the chamber then give off a decay radiation (light) characteristic for SO_2. This radiation is allowed to pass selectively through a second filter to impinge on a photomultiplier tube. The light emissions are processed electronically, such that the light energy is converted into a voltage signal which is proportional to the concentration of sulphur dioxide in the sample being analyzed. This method is highly specific, with few interferences.

3.2 Sulphuric Acid Mist (H_2SO_4)

Monitoring was undertaken for sulphuric acid mist, using NIOSH method P&CAM 187.[8] A sequential sampling system was used to draw ambient air through an impinger system containing distilled water at a rate of 1.5 L/min over a period of one hour. Samples collected were submitted to the W. M. Ward Technical Services Laboratory for analysis of total sulphate concentration. This parameter has been used in a number of jurisdictions for measurement of ambient sulphuric acid concentrations.[9, 10, 11]

3.3 Wind Speed and Direction

Wind speed and direction were obtained from an on board meteorological tower. The tower with a Windflow 540 wind speed and direction sensing instrument, manufactured by the Athabasca Research Corporation Ltd., was raised to a 10 metre height. Wind speeds were recorded on strip charts during the monitoring program. The output from the anemometer is a voltage, and was converted to appropriate engineering units (i.e. km/hr). The same principle applied to the wind direction. Directions are given relative to true north taking into account the magnetic declination of approximately 5° east in the vicinity of Winnipeg.

4. MONITORING SITES

Monitoring was conducted at three sites during the course of the survey. All locations were 0.5 km or less from the Border Chemical plant.

A detailed site description of each location accompanies Map 1[12] in Appendix A.

5. RESULTS

Hourly averaged concentrations for sulphur dioxide and sulphuric acid mist measured at each sampling site are shown in Table 2. Corresponding wind speed and direction data were measured on site.

Hourly averages were calculated for sulphur dioxide, using 12-5 minute average concentrations obtained by visual averaging of the strip chart record. Acid mist concentrations were calculated based upon total sulphate concentrations measured from analyzed samples submitted to the W. M. Ward Technical Services Laboratory.

A summary of sampling duration and average concentrations of sulphur dioxide and sulphuric acid mist are shown for each site in Table 3. Survey date is further summarized for comparison of downwind versus background levels in Table 5.

TABLE NO. 2

MONITORING RESULTS

Time (hours)	Site No.	SO_2 Conc. (ppm) 1 hr. TWA	H_2SO_4 Conc. ($\mu g/m^3$)	Wind Dir.	Wind Speed
July 4/84					
12:00-13:00	1	0.39	N.D.	263	27
13:00-14:00		0.14	N.D.	263	26
14:00-15:00		0.17	703	263	27
15:00-16:00		0.01	63	263	28
16:00-17:00		0.17	1078	263	25
17:00-18:00		0.16	1312	263	25
18:00-19:00		0.73	3766	257	23
19:00-20:00		0.56	3297	252	19
20:00-21:00		0.01	<30	202	13
21:00-22:00		0.75	3526	variable	calm
22:00-23:00		0.01	78	variable	calm
23:00-24:00		<0.01	<30	290	10
July5/84					
00:00- 1:00		0.01	63	263	13
1:00- 2:00		0.13	766	252	13
2:00- 3:00		0.15	266	268	13
3:00- 4:00		N.D.	766	272	9
4:00- 5:00		N.D.	<30	230	9
5:00- 6:00		N.D.	<30	209	13
6:00- 7:00		N.D.	78	187	13
7:00- 8:00		N.D.	<30	220	9
8:00- 9:00		N.D.	<30	209	15
9:00-10:00		N.D.	<30	209	19
10:00-11:00		N.D.	<30	202	23
11:00-12:00	2.	<0.01	<30	202	21
12:00-13:00		<0.01	<30	191	21
13:00-14:00		0.01	47	209	25
14:00-15:00		0.05	47	209	23
15:00-16:00		0.02	63	202	17
16:00-17:00		0.01	109	214	19
17:00-18:00		0.01	109	187	27
18:00-19:00		<0.01	<30	191	27
19:00-20:00		<0.01	<30	191	21
20:00-21:00		<0.01	<30	191	calm
21:00-22:00		<0.01	<30	187	11
22:00-23:00		<0.01	<30	198	calm
23:00-24:00		<0.01	<30	220	calm

TABLE 2 (CONT.)

Time (hours)	Site No.	SO_2 Conc. (ppm) 1 hr. TWA	H_2SO_4 Conc. ($\mu g/m^3$)	Wind Dir.	Wind Speed
July 6/84					
00:00- 1:00		<0.01	<30	236	calm
1:00- 2:00		<0.01	<30	202	10
2:00- 3:00		<0.01	<30	230	calm
3:00- 4:00		<0.01	<30	240	calm
4:00- 5:00		<0.01	<30	245	calm
5:00- 6:00		<0.01	<30	236	calm
6:00- 7:00		<0.01	<30	245	calm
7:00- 8:00		<0.01	<30	245	calm
8:00- 9:00		<0.01	<30	257	calm
9:00-10:00		<0.01	<30	257	calm
10:00-11:00	2.	<0.01	N.D.	240	10
11:00-12:00		<0.01	N.D.	240	calm
12:00-13:00		<0.01	N.D.	240	calm
13:00-14:00		<0.01	N.D.	240	calm
July 17/84					
11:00-12:00	3.	0.07	63	198	13
12:00-13:00		0.03	47	191	11
13:00-14:00		0.03	47	209	10
14:00-15:00		0.04	47	198	calm
15:00-16:00		0.03	<30	191	calm
16:00-17:00		0.02	<30	220	calm
17:00-18:00		0.03	<30	240	calm
18:00-19:00		0.04	<30	236	calm
19:00-20:00		0.02	63	variable	calm
20:00-21:00		0.01	<30	variable	calm
21:00-22:00		<0.01	63	variable	calm
22:00-23:00		<0.01	47	variable	calm
23:00-24:00		<0.01	47	variable	calm
July 18/84					
00:00- 1:00		<0.01	47	9	10
1:00- 2:00		<0.01	63	360	10
2:00- 3:00		<0.01	63	9	11
3:00- 4:00		<0.01	<30	5	13
4:00- 5:00		<0.01	<30	360	13
5:00- 6:00		<0.01	47	356	13

TABLE 2 (CONT.)

Time (hours)	Site No.	SO_2 Conc. (ppm) 1 hr. TWA	H_2SO_4 Conc. ($\mu g/m^3$)	Wind Dir.	Wind Speed
July 18/84					
6:00- 700		<0.01	<30	360	13
7:00- 8:00		<0.01	<30	349	13
8:00- 9:00		<0.01	<30	344	15
9:00-10:00		<0.01	47	333	17
10:00-11:00		<0.01	<30	340	21
11:00-12:00		<0.01	N.D.	344	19
12:00-13:00		<0.01	47	349	25
13:00-14:00		<0.01	<30	356	29
14:00-15:00		<0.01	<30	326	25
15:00-16:00		<0.01	<30	272	25
16:00-17:00		<0.01	<30	245	23
17:00-18:00		<0.01	63	240	23
18:00-19:00		0.01	63	240	15
19:00-20:00		0.01	<30	236	19
20:00-21:00		<0.01	63	240	19
21:00-22:00		<0.01	<30	236	21
22:00-23:00		0.02	<30	214	15
23:00-24:00		0.02	<30	220	calm
July 19/84					
00:00- 1:00		0.03	<30	230	calm
1:00- 2:00		<0.01	<30	236	calm
2:00- 3:00	3.	<0.01	<30	245	calm
3:00- 4:00		<0.01	<30	240	calm
4:00- 5:00		<0.01	<30	variable	calm
5:00- 6:00		<0.01	<30	277	calm
6:00- 7:00		<0.01	<30	283	calm
7:00- 8:00		0.03	<30	237	calm
8:00- 9:00		0.09	63	230	10
9:00-10:00		0.13	234	220	10
10.00-11:00		0.14	453	214	15
11:00-12:00		0.14	515	220	19
12:00-13:00		0.17	766	214	17
13:00-14:00		0.16	312	220	19
14:00-15:00		0.08	78	214	17
15:00-16:00		0.11	172	220	17
16:00-17:00		0.09	47	225	17
17:00-18:00		0.03	<30	230	15

TABLE 2 (CONT.)

Time (hours)	Site No.	SO_2 Conc. (ppm) 1 hr. TWA	H_2SO_4 Conc. ($\mu g/m^3$)	Wind Dir.	Wind Speed
July 19/84					
18:00-19:00		0.07	63	225	13
19:00-20:00		0.08	63	191	11
20:00-21:00		<0.01	<30	202	calm
21:00-22:00		<0.01	<30	variable	calm
22:00-23:00		<0.01	<30	variable	calm
23:00-24:00		<0.01	<30	variable	calm
July 20/84					
00:00- 1:00		<0.01	<30	variable	calm
1:00- 2:00	3.	<0.01	<30	variable	calm
2:00- 3:00		<0.01	<30	75	calm
3:00- 4:00		<0.01	<30	92	calm
4:00- 5:00		<0.01	<30	52	calm
5:00- 6:00		<0.01	<30	25	calm
6:00- 7:00		<0.01	<30	59	calm
7:00- 8:00		<0.01	<30	32	calm
8:00- 9:00		<0.01	<30	32	calm
9:00-10:00		<0.01	<30	52	13

TABLE NO. 3

SURVEY DATA SUMMARY (a)

Site No.	Times and Date	No. of Hours	SO_2 Conc. (ppm)	H_2SO_4 Conc. ($\mu g/m^3$)
1	12:00 4/7/84-11:00 5/7/84	15	0.23	
		21		751
2	11:00 5/7/84-14:00 6/7/84	27	<0.01	
		23		<30
3	11:00 17/7/84-10:00 20/7/84	71	0.02	
		70		53

TABLE NO. 4

SURVEY DATA SUMMARY (b)

	SO_2	H_2SO_4
Total No. of Monitoring Hours	113	114
Downwind Monitoring (Hours)	48	48
% of Total	42.5%	42.1%
Average Downwind Concentration	0.11 ppm	396 $\mu g/m^3$
Background (not downwind) Monitoring	65	66
% of Total	55.5%	57.9%
Average Background Concentration	<0.01	<30
Total 1 Hour Exceedances	4	17
Downwind Exceedances	4	17
% of Total	100%	100%

6. DISCUSSION

Monitoring for this study was performed in two segments, July 4-6 and July 18-20, 1984. The first survey (starting July 4) was characterized by moderate winds (15-30 km/hr), with some periods which were calm (less than 10 km/hr). The plume was held close to the ground during the periods of moderate winds, and was found to rise vertically during the calm periods. Under the described conditions, sulphur dioxide concentrations were found to exceed the one hour guideline on four occasions (July 4 12:00h-0.39 ppm, 18:00h-0.73 ppm, 19:00h-0.56 ppm, 21:00h-0.75 ppm). Eleven exceedances of the sulphuric acid mist guideline were recorded, when the MMU was in a downwind venue in relationship to the plant.

The second survey was undertaken during a period of relatively calm meteorlogical conditions, with light winds (10-20 km/hr) and clear skies. Under these conditions, six exceedances of the sulphuric acid mist guideline were recorded, while the MMU was downwind of the plant. No exceedances of the sulphur dioxide guideline were observed during the second survey, although some elevated one hour sulphur dioxide levels were observed concurrently with the exceedances of the sulphuric acid mist guideline described previously.

It should be noted that the sulphuric acid data is of a preliminary nature. Very few methods currently exist for measurement of acid mist as a specific parameter, due to the difficulty of separating the sulphuric acid aerosol component from other interference in the sample. Chemical measurement of this parameter involves analysis for one of the reactive species in the molecule (i.e. hydrogen ion or sulphate ion). Current recommended analytical methods involve measurement of total sulphate (SO_4^{-2}) in the sample, as hydrolysis of other soluble acidic and basic constituents in an air sample will mask the hydrogen ion (H^+) contribution from the sulphuric acid mist present. [13]

A downwind location from the plant was determined by comparison of wind direction and compass bearing of the plant with respect to the monitoring site. This bearing, plus or minus 20°, yields the direction range within which the receptor site is considered to be downwind of the source. This is only a generalization, however, and other factors, such as distance from source to receptor, wind velocity, and variability of the horizontal wind component will influence this range. For this study, the following ranges were used:

i) Site #1 is downwind of the Border Chemical plant when the wind direction (hourly average) ranged between 242° and 282° (i.e. 262°$\pm$ 20°);

ii) Site #2 is downwind of the Border Chemical plant when the wind direction ranged between 175° and 215°;

iii) Site #3 is downwind of the Border Chemical plant when the wind direction ranged between 190° and 230°.

A comparison of Manitoba Air Quality Objectives and Guidelines with conditions monitored downwind is as follows:

(1) Number of cardinal hours (downwind) when the one hour Maximum Acceptable Level (MAL) was exceeded for sulphur dioxide was 4 out of 48 (8%);

(2) Number of cardinal hours (downwind) when the one hour MAL standard for sulphuric acid was exceeded was 17 out of 48 (35%).

7. CONCLUSIONS

Regarding the air quality measurements conducted during this study, it can be concluded that:

(1) Under meteorological conditions similar to those experienced during this study, Manitoba Air Quality Guidelines for sulphur dioxide, based upon a one hour average could be exceeded;

(2) Downwind concentrations of sulphuric acid mist could exceed guidelines, based upon a one hour average.

References

1. Sulphur Dioxide and Sulphuric Acid Mist Sampling of Absorber Stack Exhaust at Border Chemical Company Ltd., Winnipeg, Manitoba. Air Pollution Control Section, Environmental Management Division, 1978.

2. Sulphur Dioxide and Sulphuric Acid Mist Sampling of Absorber Stack Exhaust at Border Chemical Company Limited, Winnipeg, Manitoba. Air Pollution Control Section, Environmental Management Division, 1979.

3. Source Testing for Sulphur Dioxide Gas and Sulphuric Acid Mist Emissions from Border Chemical Company Ltd., Day Street and Gunn Road, Winnipeg, Manitoba, Air Pollution Control Section, Environmental Management Division, 1985.

4. Georgie, H. W., 1970. Journal of Geophysical Resources, Volume 75, pp 2365-2372, as cited in "Review of National Ambient Air Quality Objectives for Sulphur Dioxide", 1982. Subcommittee on National Air Quality Objectives.

5. Amdur, M.; Schulz, R., A. Arch. Ind. Hyg. Occup. Med. 5 (1952) p. 318

6. West, P; Shendrikar, A. D., The Determination of Sulphuric Acid Aerosol, Analytica Chimica Acta, 69 (1974). pp. 11-116.

7. Lewis, F. R.; Amdur, M. Toxicity of Atmospheric Sulphur Dioxide Decay Product. Environmental Protection Agency. North Carolina (1972) Publication No. AP-111.

8. NIOSH Manual of Analytical Methods: Volume 1, U.S. Department of Health, Education and Welfare. Public Health Service, 1977.

9. State of Missouri, 1977, Title 10 Section .010.

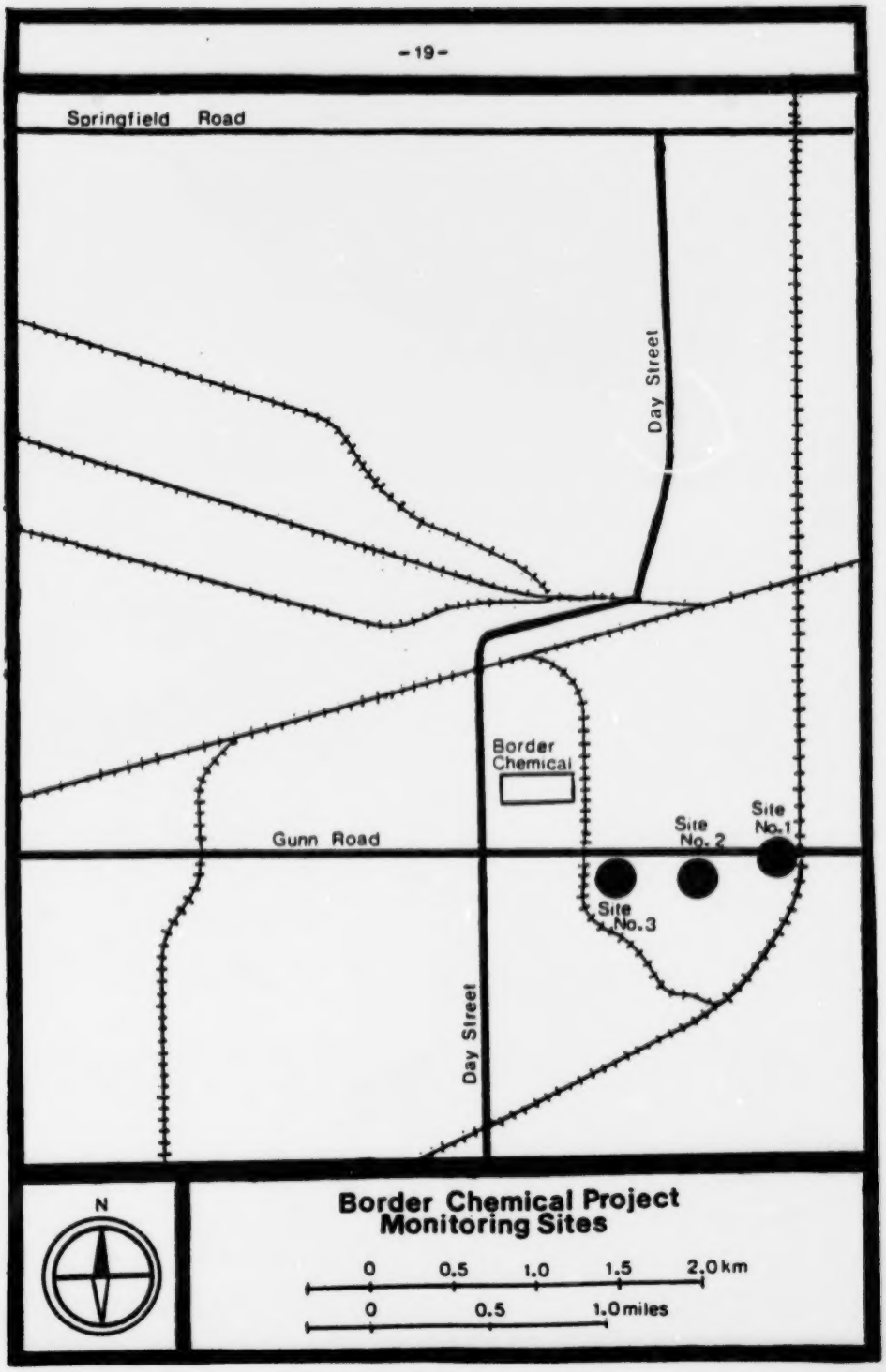
10. Province of Ontario. Regulation 308 (1982).

11. State of Pennsylvannia. S. A. C. Title 25, Part 1, Subpart C Article III - Chapter 139.

12. Map for this survey obtained from: City of Winnipeg Planning Office.

13. Dharmrajan, V.; Thomas, R., Sulphuric Acid Aerosol, The Science of the Total Environment, Vol. 4 (1975). Amsterdam. pp. 279-298.

APPENDIX


Springfield Road
Day Street
Border Chemical
Gunn Road
Site No. 2
Site No. 1
Site No. 3
Day Street
N
Border Chemical Project
Monitoring Sites
0 0.5 1.0 1.5 2.0 km
0 0.5 1.0 miles

Appendix
Monitoring Sites

Site No. 1

Description: (a) South side of Gunn Road
(b) Approximately 1.5 km east of Day Street
(c) Approximately 800 metres from Border Chemical plant.

Site No. 2

Description: (a) Warehouse South side of Gunn Road
(b) Approximately 1.2 km east of Day Street
(c) Approximately 600 km from Border Chemical plant.

Site No. 3

Description: (a) Trailer fabrication plant
(b) Approximately 700 metres east of Day Street
(c) Approximately 300 metres from Border Chemical plant